Enhancing C_2H_2/C_2H_4 separation by incorporating low-content sodium in covalent organic framework

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S1. Materials and Instrumentation.

1,2-dichlorobenzene (99%), n-butanol (99%), phloroglucinol (99%), p-phenylenediamine (99%) and trifluoroacetic acid (99%) were purchased from Macklin (Shanghai) Inc. Hexamethylenetetramine (99%) was purchased from Alfa Aesar (Beijing) Co., Ltd. All other reagents were obtained from commercial suppliers and used as received unless otherwise noted.

Power X-ray diffraction（PXRD）patterns of samples were obtained at room temperature by a Bruker D8 ADVANCE X-ray at 40 mA and 40 kV using Cu Kα (λ = 1.5405 Å) radiations form 2° to 30° (2θ angle range), the simulated powder patterns were calculated by Mercury 1.4. The N_2 adsorption-desorption isotherms were obtained at 77 K on a Belsorp-max adsorption apparatus using ultrahigh-purity-grade (>99.999%) N_2. Each sample was degassed at 110 °C for 12 h under ultrahigh vacuum before measurement. Infrared spectra (IR) were performed in Thermo Scientific Nicolet iS5 FT-IR spectrometer with the 500-4000 cm^{-1}. Scanning electron microscope (SEM) and Energy Dispersive Spectrometer (EDS) was carried out on a Hitachi S-4800 microscope. Thermal gravimetric analysis (TGA) was performed by SDT Q600 TGA instrument from 30 to 800 °C in N_2 atmosphere at a constant rate of 10 °C/min. ^{13}C NMR spectra were recorded on Bruker Avance 600 MHz spectrometer. The C_2H_2 and C_2H_4 single-component adsorption isotherms with 99.999% purity gas were carried out at 298 and 273 K water bath on a Belsorp-max adsorption apparatus after degassed at 110 °C for 12 h under ultrahigh vacuum. Elemental analysis used PerkinElmer 2400 Series II CHNS under ultrahigh-purity-grade (>99.999%) He at 975 °C.

S2. Detailed experiment

Synthesis of 2,4,6-triformylphloroglucinol: To hexamethylenetetramine (15.098 g, 108 mmol) and phloroglucinol (6.014 g, 49 mmol) under N_2 was added 90 mL trifluoroacetic acid. The solution was heated at 100 ℃ for ca. 2.5 h. Approximately 150 mL of 3 M HCl was added and the solution was heated at 100 ℃ for 1 h. After cooling to room temperature, the solution was filtered through Celite, extracted with ca. 350 mL dichloromethane, dried over magnesium sulfate, and filtered. Rotary evaporation of the solution afforded 1.23 g (5.87 mmol ,11%) of an off-white powder. ^1H NMR indicated near 99% purity; a pure sample was obtained by sublimation. ^1H NMR (400 MHz, CDCl$_3$, 25 ℃) δ14.12 (s, 1H, OH), 10.15 (s, 1H, CHO) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, 25 ℃) δ 192.01 (CHO), 173.57 (Ph-C2), 102.91 (Ph-C1) ppm. Calcd for C,51.44; H, 2.88; N, 0.00. Found: C 51.38; H 2.80; N, 0.00.
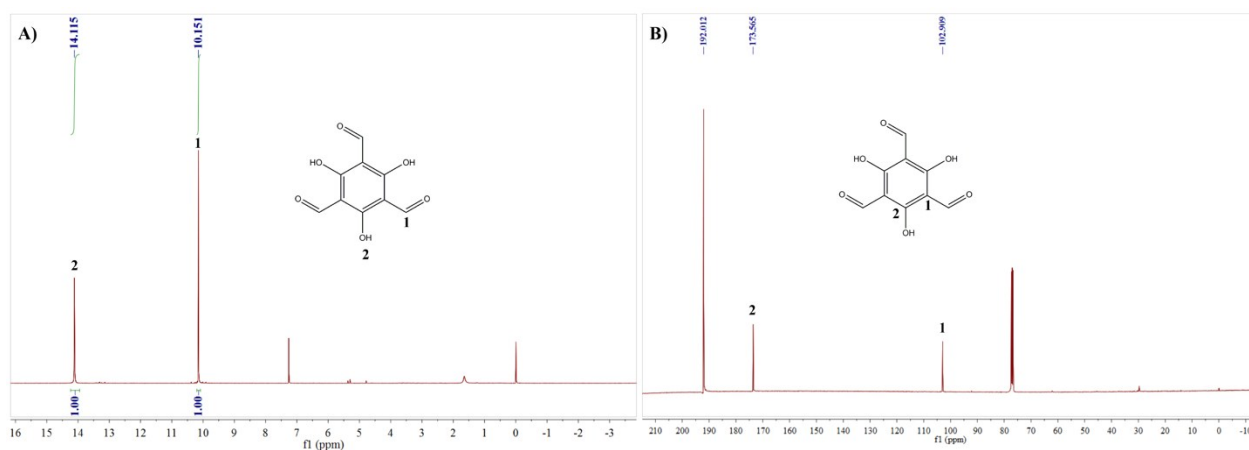
Fig. S1 A) ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) spectrum of 2,4,6-triformylphloroglucinol. B) ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C) spectrum of 2,4,6-triformylphloroglucinol.

Synthesis of 2,5-diaminobenzenesulfonic acid: To p-phenylenediamine (2.7 g, 25 mmol) was add 20% fuming sulfuric acid (33 g, 66 mmol). The solution was heated at 145 °C for ca. 7 h. Approximately 4 mL deionized water was added, and the solution was heated at 135 °C for 3 h. Cooling to 30 °C for static crystallization for 2 h. Approximately 2 mL deionized water was added and adjusted pH 4 to 5 with 30% sodium hydroxide. Cooled to 10 °C and filtered to obtain a product 3.8 g（20 mmol，80%）, HPLC purity is greater than 98%. ^{1}H NMR (400 MHz, DMSO, 25 °C) δ 7.38 (d, 1H, Ph-H1), 6.92 (dd, 1H, Ph-H3), 6.79 (d, 1H, Ph-H2), 4.55-9.10 (br., 4H, NH$_2$) ppm. ^{13}C NMR (100 MHz, DMSO, 25 °C) δ 139.50 (Ph-C4), 131.15 (Ph-C2), 123.41 (Ph-C1), 122.04 (Ph-C5), 120.56 (Ph-C6), 117.78 (Ph-C3) ppm. Calcd for C, 38.29; H, 4.28; N, 14.88; S, 17.04. Found: C 38.26; H 4.29; N, 14.83; S, 17.02.
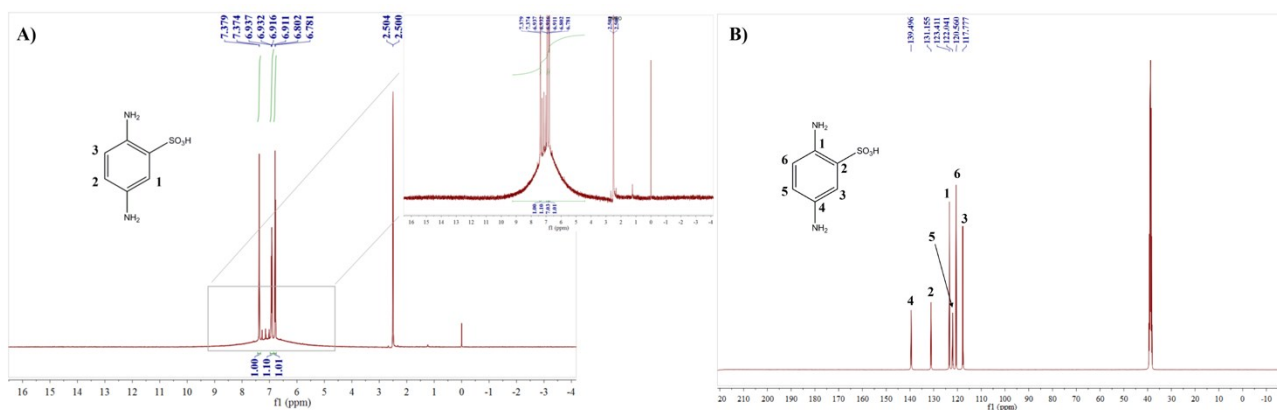

Fig. S2 A) ^{1}H NMR (400 MHz, DMSO, 25 °C) spectrum of 2,5-diaminobenzenesulfonic acid. B) ^{13}C NMR (100 MHz, DMSO, 25 °C) spectrum of 2,5-diaminobenzenesulfonic acid.

Synthesis of COF-ECUT-1. A mixture of 2,4,6-triformylphloroglucinol (63 mg, 0.3 mmol) and 2,5-diaminobenzenesulfonic acid (84.7 mg, 0.45 mmol) and a drop of n-butanol: 1,2-dichlorobenzene (1:1 v/v) was taken in Pyrex tube. The mixture was sonicated for 20 min, followed by addition of 0.5 mL of 3 M aqueous acetic acid. After that, the tube was degassed by freeze−pump−thaw cycles for three times, sealed under vacuum and heated at 120 °C for 3 days. The reaction mixture was cooled

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to room temperature and washed with deionized water, dimethylacetamide and acetone. The resulting dark red powder was dried at 60 °C under vacuum for 12 hours.

Synthesis of Na@COF-ECUT-1. 100 mg COF-SO$_3$H added in 20 mL glass bottles with 1 M sodium carbonate solution for 30 hours. Then the resulted solid samples were washed with deionized water and methanol, and further dried at 60 °C under vacuum for 12 hours.

DFT calculation method. The periodic density functional theory calculations were performed by using the Vienna Ab initio Simulation Package (VASP) code.[1] The Perdew-Burke-Ernzerhof (GGA-PBE) functional was utilized to calculate the exchange-correlation energy, and the project-augmented wave generalized gradient approximation (PAW-GGA) pseudopotentials were adopted to describe the electron-ion interaction.[2-3] All the structures were optimized aiming to the global energy minimum, fully relaxed until the residual force convergence value on each tom being less 0.05 eV/Å. The Brillouin zone was sampled by *3 x 3 x 1* Gamma k-point mesh and the wave functions were expanded using a plane-wave basis set with kinetic energy cutoff of 500 eV. Spin-polarization was calculations with the lowest energy magnetic configurations were identified. All of the above structures were established by Materials Studio.

The binding energy was calculated follow:
$$E_b = E_{*g} - E_* - E_g \times n$$
Where the E_b means binding energy, E_{*g} represents the ground state energy after loading gas molecules, the E_* is the energy of cleanly unabsorbed and the E_g is the energy of pure gas at standard conditions, n represents the number of the gas molecules are adsorbed in COF pores.[4]

Table S1. The binding energy (eV) of these COFs with loading of guest molecules.

	E_*	$E_{*C_2H_2}$	$E_{*C_2H_4}$	$E_{C_2H_2}$	$E_{C_2H_4}$	$E_b^{C_2H_2}$	$E_b^{C_2H_4}$
COF-SO$_3$H	-1144.16	-1282.34	-1336.33	-22.93	-31.96	-0.60	-0.41
COF-SO$_3$Na	-1144.45	-1284.42	-1338.30	-22.93	-31.96	-2.39	-2.09

S3. TGA curve
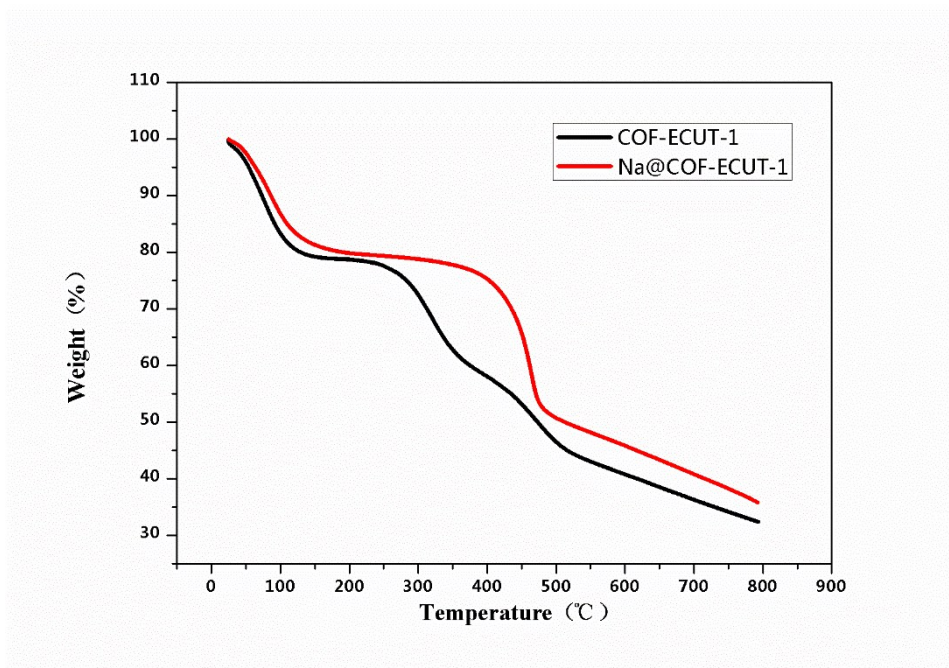
Fig. S3 TG data of **COF-ECUT-1** and **Na@COF-ECUT-1** under N_2 atmosphere.
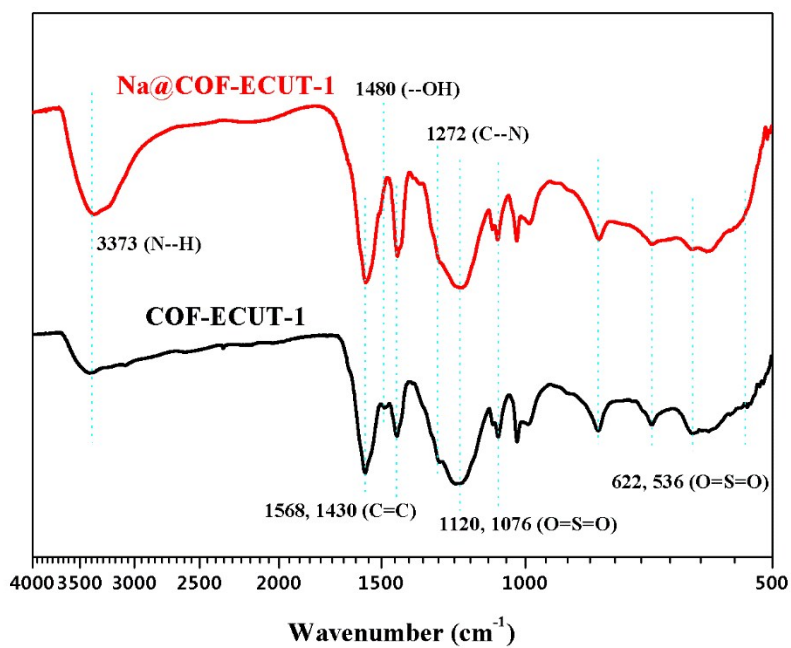

S4. FT-IR spectrum of COFs

Fig. S4 IR spectrum of **COF-ECUT-1** and **Na@COF-ECUT-1**.

S5. Solid state ^{13}C NMR spectrum of COFs
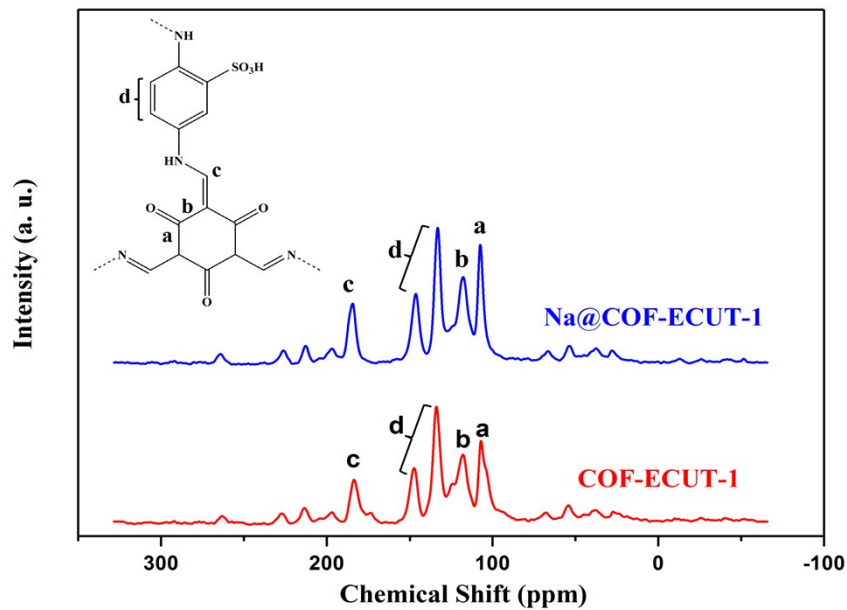

Fig. S5 ^{13}C CP/MAS NMR spectrum of **COF-ECUT-1** and **Na@COF-ECUT-1**.
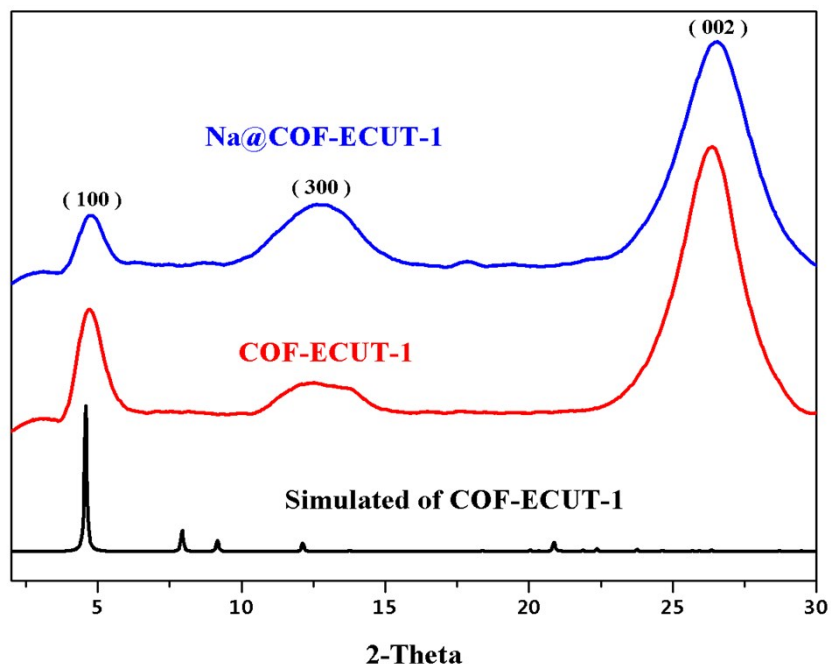
S6. XRD analysis

Fig. S6 The simulated and measured PXRD patterns of **COF-ECUT-1** and **Na@COF-ECUT-1**.
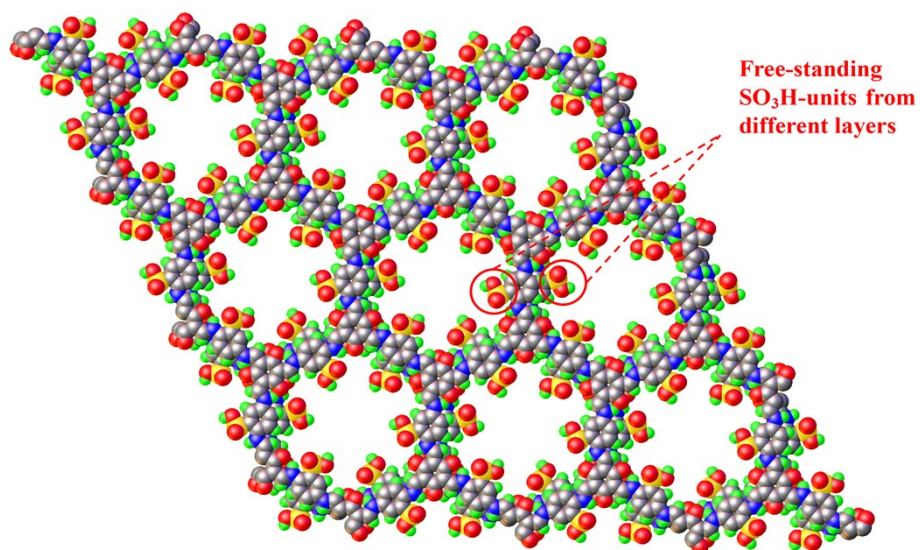
S7. View of the COF-ECUT-1 structure

Fig. S7 View of the **COF-ECUT-1** structure with free-standing SO₃H-units from different layers.
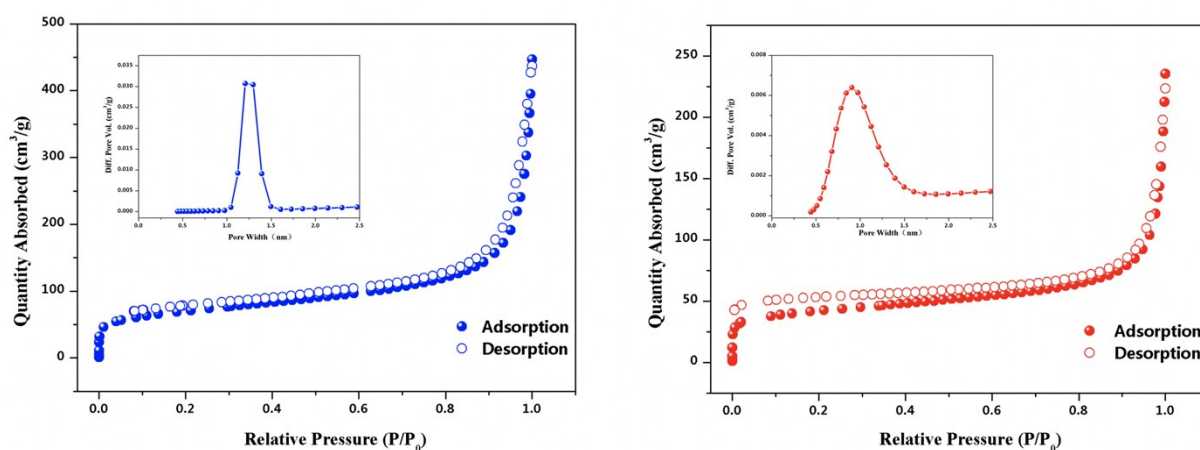
S8. Gas adsorption studies of COFs

Fig. S8 Left: N_2 adsorption-desorption isotherms (77 K) of **COF-ECUT-1** with the inset of the distribution of pore size. Right: N_2 adsorption-desorption isotherms (77 K) of **Na@COF-ECUT-1** with the inset of the distribution of pore size.

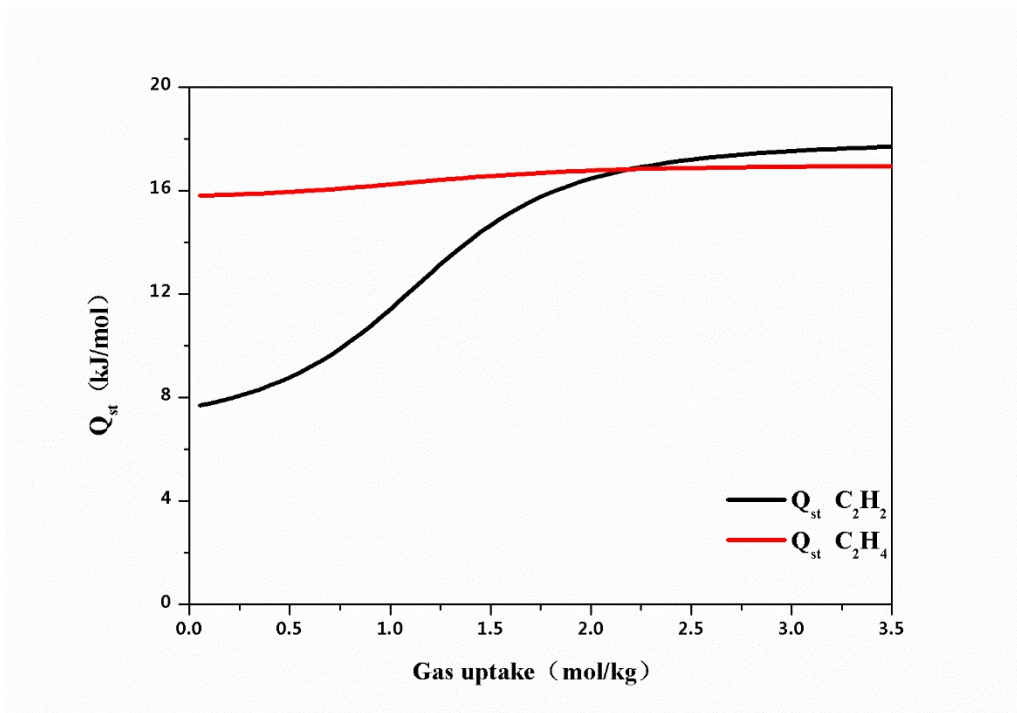## S9. Isosteric heats of adsorption of COF-ECUT-1

Fig. S9 Isosteric heats of adsorption for C_2H_2 (black) and C_2H_4 (red) of **COF-ECUT-1**.

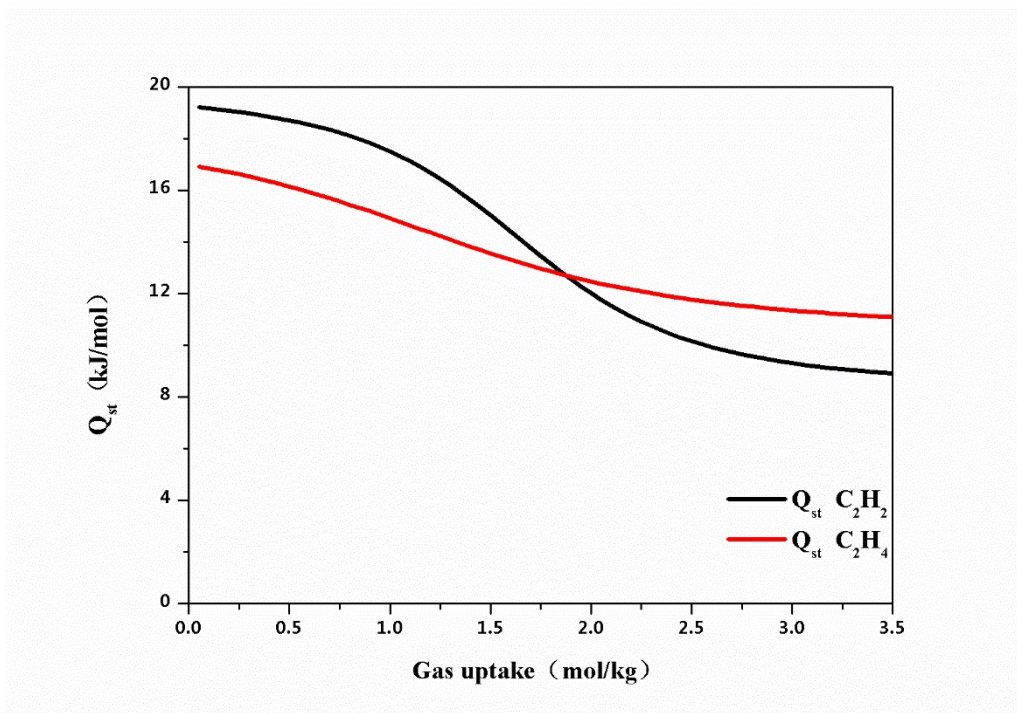## S10. Isosteric heats of adsorption of Na@COF-ECUT-1

Fig. S10 Isosteric heats of adsorption for C_2H_2 (black) and C_2H_4 (red) of **Na@COF-ECUT-1**.
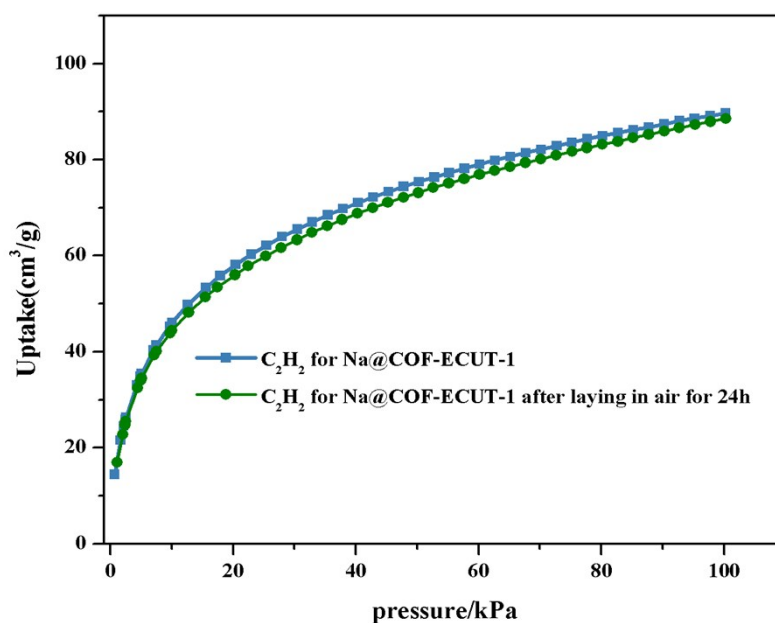
S11. Effect of moisture

Fig. S11 A comparison of C_2H_2 adsorption for the samples of **Na@COF-ECUT-1** and the counterpart after laying in air for 24 h.

S12. References

1. G. Kresse and J. Hafner, *Phys. Rev. B*, 1993, **48**, 13115-13118.
2. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456-1465.
3. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
4. O. T. Qazvini, R. Babarao, Z. L. Shi, Y. B. Zhang and S. G. Telfer, *J. Am. Chem. Soc.*, 2019, **141**, 5014-5020.